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Date of Application: September 30, 2003

Application Number: 2003-339743

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Commissioner,  
Japan Patent Office

[Name of Document] Patent Application  
 [Reference No.] WP04502  
 [Filling Date] September 30, 2003  
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 Commissioner of the Patent Office  
 [International Patent Classification] C04B 35/16  
 B01J 35/04  
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 [Payment of Fees]  
 [Advanced Payment File No.] 009689  
 [Amount of Payment] ¥21,000  
 [List of Articles Submitted]  
 [Name of Article] Scope of the Claim for Patent 1  
 [Name of Article] Specification 1  
 [Name of Article] Abstract 1  
 [General Power of Attorney No.] 9001231

[Name of Document] Scope of Claim for Patent

[Claim 1]

A method for manufacturing a honeycomb structure, the method using, as a part of a starting material, a recycled raw material recycled from a recovered material derived from the starting material of the honeycomb structure which was generated during process as for manufacturing the honeycomb structure;

wherein the recycled raw material is pulverized to have an average particle size of 10 to 2000  $\mu\text{m}$  and obtain 10% by weight or less of particles having an average particle size of 2800  $\mu\text{m}$  or more.

[Claim 2]

A method for manufacturing a honeycomb structure according to Claim 1, wherein the recycled raw material is pulverized to have an average particle size of 100 to 1000  $\mu\text{m}$  and obtain 20% by weight or less of particles having an average particle size of 45  $\mu\text{m}$  or less and 10% by weight or less of particles having particle sizes of 1400  $\mu\text{m}$  or more.

[Claim 3]

A method for manufacturing a honeycomb structure according to Claim 1 or 2, wherein the recovered material is an unfired dried material.

[Claim 4]

A method for manufacturing a honeycomb structure according to any one of Claims 1 to 3, wherein the honeycomb structure is a cordierite based honeycomb structure.

[Claim 5]

A method for manufacturing a honeycomb structure according to any one of Claims 1 to 4, the honeycomb structure having a filter structure in which both end faces of the honeycomb structure are alternately plugged in a zigzag manner.

[Claim 6]

A honeycomb structure manufactured by a method according to any one of Claims 1 to 5.

[Name of Document] Specification

[Title of the Invention] METHOD FOR MANUFACTURING HONEYCOMB  
STRUCTURE AND HONEYCOMB STRUCTURE

[Technical Field]

[0001]

The present invention relates to a method for  
manufacturing a honeycomb structure and a honeycomb  
structure.

[Background Art]

[0002]

As a filter (a diesel particulate filter (DPF)) for  
trapping and removing a particulate matter contained in a  
dust-containing fluid such as an exhaust gas from a diesel  
engine or an (exhaust gas purification) catalyst carrier for  
carrying a catalyst component for purifying harmful  
substances in the exhaust gas, a porous honeycomb structure  
is broadly used which is constituted of a plurality of cell  
partition walls (ribs) forming a complex of adjacent cells  
and a honeycomb outer wall surrounding and holding outermost  
peripheral cells positioned in the outermost periphery of  
this cell complex. Moreover, as a material constituting the  
structure, fire-resistant silicon carbide (SiC), cordierite,  
a composite material of them or the like is used.

[0003]

Moreover, the development of the DPF (the DPF for  
recycling the catalyst) has progressed in which a recycling  
system is employed for loading the oxidized catalyst on the

conventional DPF and oxidizing and burning deposited particulates to continuously perform the recycling.

[0004]

In addition, as a method for economically manufacturing the above honeycomb structure, it is preferable that a starting material composition is prepared (recycled) from a recovered material (e.g. an unfired formed body excluded for some reason in a case where a drying step shifts to a firing step, or an unfired dried body such as a piece of the unfired formed body (also including a fired body in the case of SiC)) generated in a process for manufacturing the honeycomb structure and derived from a starting material for the honeycomb structure and that the composition is reused as a recycled material in forming a formed body, from the view point of yield improvement and cost reduction.

[0005]

In the case of a cordierite ceramic structure, when an unfired dried material as the recovered material is pulverized for use as a recycled raw material, the cordierite ceramic structure manufactured by using the pulverized powder often has a larger thermal expansion coefficient in comparison with a cordierite ceramic structure manufactured by using an original starting material, and the structure has a lowered thermal impact resistance, which results in a problem that the structure cannot be used as a honeycomb catalyst carrier for purifying

the exhaust gas.

[0006]

To solve the above problems, for example, the unfired dried material as the recovered material is disintegrated, pulverized and classified in a lightly pulverizing step to use the material as the prepared (recycled) raw material (see Patent Document 1). Furthermore, at least a part of a binder contained in the unfired recycled raw material is removed from the recycled raw material, then the recycled raw material is pulverized to prepare the pulverized powder, water, the binder and the like are added to the pulverized powder, the material is kneaded to prepare a recycled kneaded clay, and the recycled kneaded clay is formed and fired (see Patent Document 2). In addition, the unfired recycled raw material is pulverized to produce a pulverized material, pieces having diameters of less than 1 mm are removed from the pulverized material, the water is added to the remaining pulverized material, the material is kneaded to produce the recycled kneaded clay, and the recycled kneaded clay is formed and fired (see Patent Document 3). Thus, the cordierite ceramic structure and the method for manufacturing the structure have been suggested.

[Patent document 1] JP-B-1703709

[Patent document 2] JP-A-2000-302533

[Patent document 3] JP-A-8-119726

[0007]

However, in the method of Patent Document 1, when the

recycled raw material is pulverized to have particle sizes of less than 10  $\mu\text{m}$ , efficiency in pulverization is poor, and not only cost is increased, but also abrasion of a pulverization device is increased, and thereby impurities are prone to get mixed.

In the method of Patent Document 2, since the recycled raw material is subjected to a thermal treatment or the like to remove the binder, manufacturing cost increases. In the method of Patent Document 3, since the recycled raw material having sizes of 1 mm or less is removed, the only small yield of the recycled raw material is obtained, and the recycled raw material is coarsely pulverized. Therefore, the kneaded material is insufficiently dissolved, and clogging or the like might be caused during the forming of the honeycomb structure.

[0008]

Moreover, to manufacture the DPF, the coarse raw material needs to be used so as to increase the porosity. However, if the recycled raw material pulverized so that the ratio of particles having an average particle size of 45  $\mu\text{m}$  or less is above 20% by weight is used, there is a problem that an average pore diameter of the resultant DPF becomes small.

[0009]

Furthermore, in a case where the DPF is manufactured, if the recycled raw material pulverized so that the ratio of particles having an average particle size of 2800  $\mu\text{m}$  or more



is above 10% by weight is used, the recycled raw material is not sufficiently dissolved in mixing and kneading steps, a die might be clogged during the forming, and cell defects might be generated in the resultant honeycomb structure.

[Disclosure of the Invention]

[Problem to be solved by the Invention]

[0010]

The present invention has been made in view of the above-mentioned problems of the conventional technology and objectives of the present invention are to provide a method for manufacturing a honeycomb structure having the same degrees of low thermal expansion coefficient and porosity as those in the case of using an original starting material and capable of achieving the improvement of yield and the considerable decrease of cost, when the honeycomb structure is manufactured by using an unfired recycled raw material (in the case of SiC, a fired material may be used) recovered in a manufacturing process of the honeycomb structure, and to provide the honeycomb structure.

[Means for solving the Problem]

[0011]

That is, according to the present invention, there is provided a method for manufacturing a honeycomb structure, the method using, as a part of a starting material, a recycled raw material recycled from a recovered material generated in a process for manufacturing the honeycomb structure and derived from the starting material of the

honeycomb structure; wherein the recycled raw material is pulverized to have an average particle size of 10 to 2000  $\mu\text{m}$  and obtain 10% by weight or less of particles having an average particle size of 2800  $\mu\text{m}$  or more.

[0012]

At this time, in the present invention, the above recycled raw material is preferably pulverized to have an average particle size of 100 to 1000  $\mu\text{m}$  and obtain 20% by weight or less of particles having an average particle size of 45  $\mu\text{m}$  or less and 10% by weight or less of particles having particle sizes of 1400  $\mu\text{m}$  or more.

[0013]

Moreover, in the present invention, the above recovered material is preferably an unfired dried material, and the honeycomb structure is preferably a cordierite based honeycomb structure.

[0014]

Furthermore, in the present invention, the honeycomb structure preferably has a filter structure in which both end faces of the honeycomb structure are alternately plugged in a zigzag manner.

[Effect of the Invention]

[0015]

In a method for manufacturing a honeycomb structure and the honeycomb structure of the present invention, when the honeycomb structure is manufactured by using a recovered material generated in a process for manufacturing the

honeycomb structure and derived from a starting material of the honeycomb structure, the honeycomb structure has the same degrees of low thermal expansion coefficient and porosity as those in the case of using an original starting material, and the improvement of yield and the considerable decrease of cost can be achieved.

[Best Mode for Carrying Out the Invention]

[0016]

A method for manufacturing a honeycomb structure according to the present invention uses, as a part of a starting material, a recycled raw material recycled from a recovered material derived from the starting material of the honeycomb structure which was generated during process as for manufacturing the honeycomb structure, and the recycled raw material is pulverized to have an average particle size of 10 to 2000  $\mu\text{m}$  and obtain 10% by weight or less of particles having an average particle size of 2800  $\mu\text{m}$  or more.

This is because, when the recycled raw material is pulverized to have an average particle size of less than 10  $\mu\text{m}$ , efficiency in pulverization is poor, and not only cost is increased, but also abrasion of a pulverization device is increased, and thereby impurities are prone to get mixed.

Moreover, when the ratio of particles having an average particle size of 2800  $\mu\text{m}$  or more in the recycled raw material is above 10% by weight, the recycled raw material is not sufficiently dissolved in mixing and kneading steps, a die might be clogged during the forming, and cell defects

might be generated in the resultant formed honeycomb body. Moreover, the coefficient of thermal expansion (CTE) of the resultant honeycomb structure after firing (a fired body) increases.

[0017]

At this time, in the present invention, the recycled raw material is more preferably pulverized to have an average particle size of 50 to 1000  $\mu\text{m}$  and obtain 20% by weight or less of particles having an average particle size of 45  $\mu\text{m}$  or less and 10% by weight or less of particles having particle sizes of 1400  $\mu\text{m}$  or more.

This is because, in a case where the recycled raw material is used as a DPF material, when the ratio of the particles having an average particle size of less than 45  $\mu\text{m}$  is above 30% by weight, the average pore diameter of the resultant DPF decreases.

[0018]

Moreover, in the present invention, the starting material in the process for manufacturing the honeycomb structure preferably contains 1 to 70% by weight of the recycled raw material.

This is because, when the ratio of the recycled raw material is above 70% by weight, the raw material particles have abnormal reactivity due to pulverizing, and the thermal expansion coefficient might increase.

[0019]

Furthermore, in the present invention, the recovered

material derived from the starting material of the honeycomb structure which was generated during process as for manufacturing the honeycomb structure is preferably an unfired dried material.

This is because, when the cordierite based honeycomb structure is manufactured, it is indispensable to use a cordierite forming raw material as the recycled raw material.

Moreover, when a silicon carbide based honeycomb structure is manufactured, the recycled raw material may be an unfired dried material or a fired material.

Furthermore, when the above-mentioned recovered material is an undried material, the material is preferably sufficiently dried for use.

[0020]

As described above, in the method for manufacturing the honeycomb structure of the present invention, when the honeycomb structure is manufactured by using the recovered material derived from the starting material of the honeycomb structure which was generated during process as for manufacturing the honeycomb structure, the honeycomb structure has the same degrees of low thermal expansion coefficient and porosity as those in the case of using the original starting material, and the improvement of yield and the considerable decrease of cost can be achieved.

Moreover, the method for manufacturing the honeycomb structure of the present invention is preferably usable not only in an (exhaust gas purification) catalyst carrier for

carrying a catalyst component for purifying harmful substances in an exhaust gas but also in a DPF having a filter structure in which both end faces of the honeycomb structure are alternately plugged in a zigzag manner.

[Examples]

[0021]

The present invention will hereinafter be described in more detail on the basis of Examples. However, the present invention is by no means limited to these examples.

[0022]

(Examples 1 to 3, Comparative Examples 1 and 2, Reference Example 1)

A honeycomb dried body using a cordierite forming raw material for a DPF was coarsely pulverized with a hammer mill and then pulverized with a roll crusher, and sieving was conducted if necessary to obtain recycled raw materials described in Table 1. Next, starting materials in which 30% by weight of recycled raw material was added to 70% by weight of the cordierite forming raw material were prepared, a binder was added to each of the materials, and the material was mixed with a ploughshare mixer for three minutes. A pore-forming material was added to the material, and the material was mixed with the ploughshare mixer for three minutes. Furthermore, water in the form of mist was added to the material, the material was mixed for three minutes, and the resultant mixture was kneaded with a sigma type kneader for 60 minutes to obtain a kneaded clay. The

resultant kneaded clay was further kneaded with a vacuum clay kneader to obtain a cylindrical kneaded clay, and the kneaded clay was subjected to extrusion forming with a ram type extruder to obtain a honeycomb formed body, which was then subjected to microwave drying, followed by hot air drying to obtain a honeycomb dried body. The resultant honeycomb dried body was cut into a predetermined dimension, and both end faces of the body were alternately plugged in a zigzag manner with a slurry plugging material of the cordierite forming raw material. The resultant body was fired at 1420°C for six hours, thereby obtaining DPFs (a cell structure: a rib thickness of 0.3 mm, a cell density of 47 cells/cm<sup>3</sup>, a size:  $\phi$ 229 mm  $\times$  L254 mm) (Examples 1 to 3, Comparative Examples 1 and 2).

Moreover, a DPF was obtained by using 100% of cordierite forming raw material for the DPF as a starting material by a manufacturing method similar to the above method (Reference Example 1). The characteristics of the resultant DPF are shown in Table 1.

[0023]

It is to be noted that as the cordierite forming raw material for the DPF, there was used a composition containing 10 to 30% by weight of kaolin having an average particle size of 5 to 10  $\mu$ m, 37 to 41% by weight of talc having an average particle size of 20 to 30  $\mu$ m, 10 to 20% by weight of aluminum hydroxide having an average particle size of 2 to 5  $\mu$ m, 10 to 20% by weight of aluminum oxide having

an average particle size of 4 to 8  $\mu\text{m}$ , and 5 to 20% by weight of melted silica or quartz having an average particle size of 20 to 50  $\mu\text{m}$ .

[0024]

[Table 1]

	Particle size distribution of recycled raw material				Honeycomb characteristics			
	Average particle size ( $\mu\text{m}$ )	45 $\mu\text{m}$ or less (weight %)	1400 $\mu\text{m}$ or more (weight %)	2800 $\mu\text{m}$ or more (weight %)	Average pore diameter ( $\mu\text{m}$ )	Porosity (%)	Thermal expansion coefficient ( $\times 10^{-6}/^{\circ}\text{C}$ )	No. of cell defects (defects)
Example 1	100	20	0.5	0.0	22	59	0.6	0
Example 2	500	4	1.0	0.0	23	59	0.6	0
Example 3	1000	2	10.0	4.0	24	60	0.6	0
Comparative Example 1	7	92	0.0	0.0	14	58	0.8	0
Comparative Example 2	3200	1	73.0	57.0	27	65	0.8	6
Reference Example 1	-	-	-	-	23	59	0.6	0

[0025]

(Examples 4 to 6, Comparative Examples 3 and 4, Reference Example 2)

A honeycomb dried body using a cordierite forming raw material for purifying an exhaust gas from a gasoline engine was pulverized with a roll crusher and then pulverized with a disinter, and sieving was conducted if necessary to obtain recycled raw materials described in Table 2. Next, starting materials in which 30% by weight of recycled raw material was added to 70% by weight of the cordierite forming raw material were prepared, a binder was added to each of the materials, and the material was mixed with a ploughshare mixer for five minutes. Furthermore, water in the form of mist was added to the material, the material was mixed with the ploughshare mixer for five minutes, and the resultant mixture was formed into a honeycomb shape with a biaxial



continuous forming machine. The resultant honeycomb formed body was subjected to microwave drying, followed by hot air drying to obtain a honeycomb dried body. The resultant honeycomb dried body was cut into a predetermined dimension, and was fired at 1420°C for four hours, thereby obtaining honeycomb structures (a cell structure: a rib thickness of 0.05 mm, a cell density of 140 cells/cm<sup>3</sup>, a size:  $\phi$ 103 mm × L129 mm) (Examples 4 to 6, Comparative Examples 3 and 4).

Moreover, a honeycomb structure was obtained by using 100% of cordierite forming raw material for purifying the exhaust gas from the gasoline engine as a starting material by a manufacturing method similar to the above method (Reference Example 2). The characteristics of the resultant honeycomb structure are shown in Table 2.

[0026]

It is to be noted that as the cordierite forming raw material for purifying the exhaust gas from the gasoline engine, there was used a composition containing 0 to 40% by weight of kaolin having an average particle size of 2 to 10  $\mu$ m, 37 to 41% by weight of talc having an average particle size of 5 to 20  $\mu$ m, 0 to 25% by weight of aluminum hydroxide having an average particle size of 0.5 to 5  $\mu$ m, 0 to 25% by weight of aluminum oxide having an average particle size of 2 to 8  $\mu$ m, and 0 to 25% by weight of melted silica or quartz having an average particle size of 3 to 20  $\mu$ m.

[0027]

[Table 2]

	Particle size distribution of recycled raw material				Honeycomb characteristics			
	Average particle size (μm)	45 μm or less (weight %)	1400 μm or more (weight %)	2800 μm or more (weight %)	Average pore diameter (μm)	Porosity (%)	Thermal expansion coefficient (×10 <sup>-6</sup> /°C)	No. of cell defects (defects)
Example 4	10	90	0.0	0.0	3	34	0.6	0
Example 5	500	5	2.0	0.5	3	34	0.5	0
Example 6	2000	1	17.0	10.0	3	34	0.5	0
Comparative Example 3	6	93	0.0	0.0	3	34	0.8	4
Comparative Example 4	3300	1	25.0	16.0	12	39	0.8	12
Reference Example 2	-	-	-	-	3	34	0.5	0

[0028]

It is to be noted that the measurement of the particle size distribution of the recycled raw material was performed by a method as follows.

The particles having an average particle size of 45 μm or more were measured by a JIS standard sieve.

The particles having an average particle size of 45 μm or less were measured with a particle size distribution measuring instrument (LA-910 manufactured by Horiba, Ltd.) by a laser diffraction method.

[0029]

Moreover, the honeycomb characteristics were measured by a method as follows.

(1) Average Pore Diameter

A pore distribution and an average pore diameter were measured by a mercury intrusion porosimeter manufactured by Micromeritics Co.

(2) Porosity

The true specific gravity of cordierite was set to 2.52 g/cc, and the porosity was calculated from the total

pore volume.

(3) Thermal Expansion Coefficient

The honeycomb fired body was cut in a flow path direction, and the thermal expansion coefficient in a range of 40 to 800°C was measured.

(4) Number of Cell Defects

Fifty honeycomb structures were continuously formed, and the number of cell defects of the 51st honeycomb structure was counted.

[0030]

(Considerations: Examples 1 to 3, Comparative Examples 1 and 2, Reference Example 1)

As shown in Table 1, in Examples 1 to 3, the resultant honeycomb characteristics satisfactorily bear even in comparison with Reference Example 1.

On the other hand, in Comparative Example 1, since the raw material for the DPF was minutely pulverized to obtain an average particle size of up to 7  $\mu\text{m}$ , the average pore diameter of the honeycomb structure was as small as 14  $\mu\text{m}$ . Moreover, the thermal expansion coefficient thereof increased to  $0.8 \times 10^{-6}/^{\circ}\text{C}$ . This is supposedly because the raw material particles had abnormal reactivity due to pulverizing minutely.

It is considered that in Comparative Example 2, since the recycled raw material was coarsely pulverized, the recycled raw material was not sufficiently dissolved during the mixing and kneading, the average pore diameter, porosity

and thermal expansion coefficient increased, and thereby the cell defects were generated.

[0031]

(Considerations: Examples 4 to 6, Comparative Examples 3 and 4, Reference Example 2)

As shown in Table 2, in Examples 4 to 6, the resultant honeycomb characteristics satisfactorily bear even in comparison with Reference Example 2.

On the other hand, it is considered that in Comparative Example 3, the cell defects are generated because the minutely pulverized powder got mixed with abraded powder from the pulverization defects. Moreover, it is considered that the thermal expansion coefficient thereof increased because the raw material particles had the abnormal reactivity due to pulverizing minutely.

It is considered that in Comparative Example 4, since the recycled raw material was coarsely pulverized in the same manner as in Comparative Example 2, the recycled raw material was not sufficiently dissolved, the average pore diameter, porosity and thermal expansion coefficient increased, and thereby the cell defects were generated.

[Industrial Applicability]

[0032]

The present invention can suitably be applied to manufacture of a filter (a diesel particulate filter (DPF)) for trapping and removing a particulate matter contained in a dust-containing fluid such as an exhaust gas from a diesel

engine or an (exhaust gas purification) catalyst carrier for carrying a catalyst component for purifying harmful substances in the exhaust gas.

[Name of Document] Abstract

[Abstract]

[Theme] To provide a method for manufacturing a honeycomb structure having the same degrees of low thermal expansion coefficient and porosity as those in the case of using an original starting material and capable of achieving the improvement of yield and the considerable decrease of cost, when the honeycomb structure is manufactured by using an unfired recycled raw material (in the case of SiC, a fired material may be used) recovered in a manufacturing process of the honeycomb structure, and to provide the honeycomb structure.

[Means] There are disclosed a method for manufacturing a honeycomb structure, the method using, as a part of a starting material, a recycled raw material recycled from a recovered material derived from the starting material of the honeycomb structure which was generated during process as for manufacturing the honeycomb structure, and a honeycomb structure. The recycled raw material is pulverized to have an average particle size of 10 to 2000  $\mu\text{m}$  and obtain 10% by weight or less of particles having an average particle size of 2800  $\mu\text{m}$  or more.

[Adopted Figure] None

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VERIFICATION

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do hereby verify that I am fully conversant with the Japanese and English  
languages and that attached translation signed by me is, to the best of my  
knowledge and belief, a true and correct English translation of the Japanese  
Patent Application No. 2003-339743.

DATED December 5, 2008

SIGNED

K. Watanabe